

ADVANCED FUEL CELL DEVELOPMENT

**Progress Report for
July–September 1977**

by

**J. P. Ackerman, K. Kinoshita, J. W. Sim,
R. Swaroop, and P. A. Nelson**

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Argonne, Illinois 60439

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Chemical Engineering Division

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CHEMICAL ENGINEERING DIVISION
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ABSTRACT

This report describes advanced fuel cell research and development activities at Argonne National Laboratory (ANL) during the period July–September 1977. This work has been aimed at understanding and improving the performance of fuel cells having molten alkali-carbonate mixtures as electrolytes; the fuel cells operate at temperatures near 923 K.

The largest part of this effort has been directed toward development of methods for fabricating and evaluating electrolyte structures for these cells and optimizing their design. Cell performance, life, and cost are the criteria of optimization. During this period, the low-temperature synthesis of rodlike β - LiAlO_2 for the electrolyte tile has been accomplished using inexpensive (\$0.16/kg or \$0.073/lb) alumina as the starting material, thereby reducing the alumina cost by a factor of twenty-seven.

The intent of cell testing is to evaluate components under operating conditions that are as typical of the state of the art as possible. The present cells (7-cm-dia, cylindrical) have Type 316 stainless steel housings and current collectors, nickel anodes, and nickel oxide cathodes. During this quarter, a clear relationship has been established between electrolyte structure and cell performance, and the effectiveness of a wet-seal protection technique has been demonstrated for more than 2600 h.

A satisfactory method for testing of electrolyte specimens for thermal expansion and high-temperature static creep has been developed. Results for the first few samples are given, and a tentative preliminary correlation with conventional creep behavior is proposed.

SUMMARY

Electrolyte Development

Preparation and Characterization of Electrolytes. The low-temperature synthesis of rodlike β -LiAlO₂ using Alcoa C-33 alumina as the starting material has yielded results equivalent to those obtained with a starting material of Type C alumina from Degussa, Inc. The cost of alumina is reduced by a factor of twenty-seven, since C-33 alumina, which is of a type that is widely available, costs only \$0.16/kg (\$0.0725/lb). The use of mixtures of rodlike β -LiAlO₂ with other types of LiAlO₂ appears to be desirable in electrolyte structures (tiles), and several methods for making these mixtures are under study.

Phase and Structural Stability of LiAlO₂. The stability of β -LiAlO₂ at 923 K in air and in a simulated fuel environment has been demonstrated for more than 2400 h in continuing tests. In both tests, the rodlike β -LiAlO₂ particles, mixed with 55 wt % of Li₂CO₃/K₂CO₃, have retained their shape and allotropic composition. This contrasts with a previously observed transformation to γ -LiAlO₂ at 973 K. The stability of β -LiAlO₂ at 923 K has been confirmed in short-term (\sim 700-h) tests in operating cells.

Cell Testing

Cell Operation. During this quarter, cell testing has established a clear relationship between cell performance and the form of the LiAlO₂ particles in the electrolyte tile; moreover, the tests have indicated that a fairly broad range of LiAlO₂ particle sizes is required. The better cells yielded power densities of \sim 110 mW/cm² at 10-A gas flows and 60% conversion.

Wet Seal Protection. The aluminizing technique for wet-seal protection looks attractive after 2600 h in five consecutive cell tests.

Component Analysis and Development

Tile Diagnostics. The tile creep rates measured for the first few samples were from 30 to 67 x 10⁻⁶ h⁻¹ at 93 kPa load and 923 K. The time dependence of creep rate was compared with conventional behavior of "elastic" materials.

Corrosion Studies. A cell clad with Type 310 stainless steel foils was operated for 200 h. Anode and cathode wet-seal corrosion were 30 x 10⁻³ and 8 x 10⁻³ mm, respectively.

I. INTRODUCTION

The advanced fuel cell studies at Argonne National Laboratory (ANL) are part of the ERDA Second Generation Fuel Cell Program. The goal of this ERDA program is the earliest possible introduction of high-efficiency generating systems based on molten-carbonate fuel cells, which have the capability of operating on coal or other fuels. At the present stage of development, the primary thrust of the program is directed to development of the fuel cell itself.

A molten carbonate fuel cell consists of a porous metal anode (presently nickel or an alloy of nickel), a porous nickel oxide cathode, an electrolyte structure which separates the anode and cathode and conducts only ionic current between them, and appropriate metal housings or, in the case of stacks of cells, intercell separator plates. The cell housings (or separator plates) bear upon the electrolyte structure to form a seal between the environment and the anode and cathode gas compartments. The electrolyte structure, which is commonly called a "tile," is a composite structure of solid LiAlO_2 particles and a mixture of alkali metal carbonates which are liquid at the cell operating temperature of 923 K. At the anode, hydrogen and carbon monoxide in the fuel gas react with carbonate ion from the electrolyte to form carbon dioxide and water, giving up electrons to the external circuit. At the cathode, carbon dioxide and oxygen react and accept electrons from the external circuit to re-form carbonate ion, which is conducted through the electrolyte to the anode. In a practical cell stack, CO_2 for the cathode would be obtained from the anode exhaust.

The ANL contribution to the program is intended to provide understanding of cell behavior and to develop improved components and processes. More improvements are needed in the electrolyte tile than in any other single component. For this reason, electrolyte development is receiving special attention at ANL. Characterization of tile properties and the relation of the properties to tile behavior in cells is of major importance. Determination of the stability of tile materials is also of high priority.

Operation of cells is required for assessment of the behavior of tiles and other components and for understanding of the performance and life-limiting mechanisms at work within the cell. Cell operation is, of course, coupled with a diagnostic effort and a materials-development effort, with the aim of developing cells of adequate performance and longevity for realistic component testing.

II. ELECTROLYTE DEVELOPMENT

A. Preparation and Characterization of Electrolytes

The compatibility between the pore-size distributions of the molten carbonate/ LiAlO_2 matrix and the porous electrode is one important consideration in optimizing the performance of molten carbonate fuel cells. As part of the research and development effort to improve the performance of molten carbonate fuel cells, we have focused our attention on the preparation and characterization of samples of LiAlO_2 and the testing of these materials in electrolyte structures under realistic operating conditions. This study has involved the preparation of LiAlO_2 with well-defined particle morphology and the correlation of this property with the performance of molten-carbonate fuel cells containing these materials.

Previously (ANL-77-29, ANL-77-56), we showed that $\beta\text{-LiAlO}_2$ with a rodlike particle shape can be routinely prepared by the reaction of LiOH and $\gamma\text{-Al}_2\text{O}_3$ in the presence of KOH . In these preparations, we have used $\gamma\text{-Al}_2\text{O}_3$ (Type C) obtained from Degussa, Inc., which has a small particle diameter ($0.01\ \mu\text{m}$ average), large surface area ($100 \pm 15\ \text{m}^2/\text{g}$), and high chemical purity. One potential disadvantage of using Degussa Al_2O_3 for mass

production of LiAlO_2 for commercial fuel cell applications may be its relatively high cost, which is currently \$6.72/kg (\$3.05/lb) for orders of 13,200 kg (6000 lb) or more. Thus, alternative sources of alumina are being considered which are less costly than Degussa Al_2O_3 , while still yielding rodlike $\beta\text{-LiAlO}_2$ particles when reacted with LiOH in the presence of KOH . Hydrated alumina (C-33), a white granular powder obtained from Aluminum Company of America (Alcoa), was examined as a substitute for Degussa Al_2O_3 . X-ray diffraction analysis of the hydrated alumina indicated that the powder was $\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (called gibbsite*). For a shipment of 88,100 kg (40,000 lb), the cost is \$0.16/kg (\$0.0725/lb), about twenty-seven times less than the cost of Degussa Al_2O_3 , even taking into account that hydrated alumina is approximately 35 wt % H_2O .

A sample of LiAlO_2 was synthesized from a mixture of LiOH , KOH , and hydrated alumina by the procedure outlined previously (ANL-77-29, pp. 4-11; ANL-77-56, pp. 3-5). Briefly, $\text{LiOH/KOH/Al}(\text{OH})_3$, initially at room temperature, was treated with CO_2 for 1.5 h. After grinding, the sample was further treated with CO_2 at 773-973 K for 2 h to remove water and to complete carbonation of any unreacted hydroxides.

Scanning electron microscopy (SEM) showed that well-defined rodlike particles of $\beta\text{-LiAlO}_2$ were obtained. The rodlike particles have diameters which vary from about 0.5 to 1 μm and aspect ratios (length/diameter) of about 3. These dimensions are remarkably similar to the dimensions of the rodlike $\beta\text{-LiAlO}_2$ obtained when Degussa Al_2O_3 is the starting material in this same synthesis. The synthesis of $\beta\text{-LiAlO}_2$ from hydrated alumina is encouraging in that it demonstrates the feasibility of producing rodlike $\beta\text{-LiAlO}_2$ particles from an aluminum oxide other than the high-surface-area, small-particle-size Degussa Al_2O_3 . However, no electrolyte tiles have been prepared yet from the $\beta\text{-LiAlO}_2$ obtained from hydrated alumina.

The powders containing $\beta\text{-LiAlO}_2$ prepared from the hydrated alumina form a paste upon heating to about 793 K, but the paste becomes a molten slurry after about five minutes. When Degussa Type C alumina is used in this same synthesis, the paste forms but does not break down into a slurry.

When a sample is prepared by reaction of Degussa Type C alumina with Li_2CO_3 and K_2CO_3 to yield $\alpha\text{-LiAlO}_2$, it does not form a paste but rather remains frangible and fluffy, and shows very little consolidation. As is described in Section III below, the fluffy powders, when pressed, yield electrolyte tiles which perform better in our cells than tiles made from the samples containing only rodlike $\beta\text{-LiAlO}_2$. Furthermore, the tiles pressed from the rodlike $\beta\text{-LiAlO}_2$ tend to be soft and easily deformed in the cell. These observations suggest that electrolyte is less tenaciously retained by tiles containing only the uniform, rodlike $\beta\text{-LiAlO}_2$ particles than by those containing $\alpha\text{-LiAlO}_2$.

* Upon heating, gibbsite transforms to boehmite, $\text{AlO}(\text{OH})$, which transforms to $\gamma\text{-Al}_2\text{O}_3$ with the loss of H_2O .

Examination of the LiAlO_2 phase by scanning electron microscopy shows that the rodlike $\beta\text{-LiAlO}_2$ is remarkably uniform in particle size and shape, whereas the $\alpha\text{-LiAlO}_2$ has a variety of particle sizes of ill-defined shape. We believe that a fairly broad size distribution of LiAlO_2 particles yields tiles which retain electrolyte strongly and therefore also have good resistance to deformation. The ideal tile may well contain a mixture of the rodlike particles for mechanical strength and some LiAlO_2 of a wide spectrum of sizes for electrolyte retention.

Several approaches are being considered for synthesizing mixtures of rod-shaped $\beta\text{-LiAlO}_2$ particles and high-surface-area LiAlO_2 particles with different shapes (clumps, spheres, bipyramids) for testing in molten carbonate fuel cells. Table 1 briefly summarizes the procedures used to prepare LiAlO_2 /electrolyte mixtures. Three mixtures were examined with the aim of producing $\beta\text{-LiAlO}_2$ rod-shaped particles starting with $\text{LiOH/KOH}/\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-LiAlO}_2$ clumps starting with $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$. Sample 98-7 was a mixture of 50:50 wt % $\beta\text{-LiAlO}_2$ and $\alpha\text{-LiAlO}_2$, which had been prepared separately. As expected, SEM analysis showed that the rod-shaped $\beta\text{-LiAlO}_2$ particles and the $\alpha\text{-LiAlO}_2$ clumps were present as discrete separate particles.

Table 1. Preparation of Mixtures of Allotropes of LiAlO_2

Sample	Starting Materials ^a		Treatment of Mixture			LiAlO_2 Phase
	Powder 1	Powder 2	Temp., K	Time, h	Gas	
98-7	$\beta\text{-LiAlO}_2/\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$	$\alpha\text{-LiAlO}_2/\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$	-	-	-	$\alpha\text{-LiAlO}_2$ $\beta\text{-LiAlO}_2$
98-14	$\text{LiOH/KOH}/\gamma\text{-Al}_2\text{O}_3$	$\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$	296	4	CO_2	$\beta\text{-LiAlO}_2$ (major)
			773	2	CO_2	$\beta\text{-LiAlO}_2$ (major)
98-18	$\text{LiOH/KOH}/\gamma\text{-Al}_2\text{O}_3$	$\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$	296	5	CO_2	$\beta\text{-LiAlO}_2$ (major), $\gamma\text{-Al}_2\text{O}_3$ (possibly)
			773	2.5	CO_2	$\beta\text{-LiAlO}_2$ (major), $\alpha\text{-LiAlO}_2$ or $\gamma\text{-Al}_2\text{O}_3$ (minor)

^a Al_2O_3 used was Degussa, Type C.

Sample 98-18 was prepared from a mixture similar to Sample 98-7; however, the starting material was a 50:50 wt % mixture of *unreacted* powders (Powders 1 and 2 in Table 1). The two powders were physically mixed and then treated with CO_2 at 296 K to convert the hydroxides to carbonates and to promote formation of $\beta\text{-LiAlO}_2$. A high-temperature (773 K) treatment with CO_2 was used to convert unreacted hydroxides to carbonates, remove water, and promote reaction of Li_2CO_3 and $\gamma\text{-Al}_2\text{O}_3$ to form $\alpha\text{-LiAlO}_2$. X-ray diffraction analysis* showed $\beta\text{-LiAlO}_2$ as the major phase, but $\alpha\text{-LiAlO}_2$ could not be clearly detected due to the broadness of what are presumably the X-ray diffraction lines of the α allotrope. The scanning electron micrograph in Fig. 1 clearly shows the presence of rod-shaped particles and clump-shaped particles. Close examination of the electron micrograph indicates that the rods and clumps may be fused together, a condition that was not clearly evident in the scanning electron micrographs of Sample 98-7.

* All X-ray diffraction analyses described in this report were performed by B. S. Tani, Analytical Chemistry Laboratory, ANL.

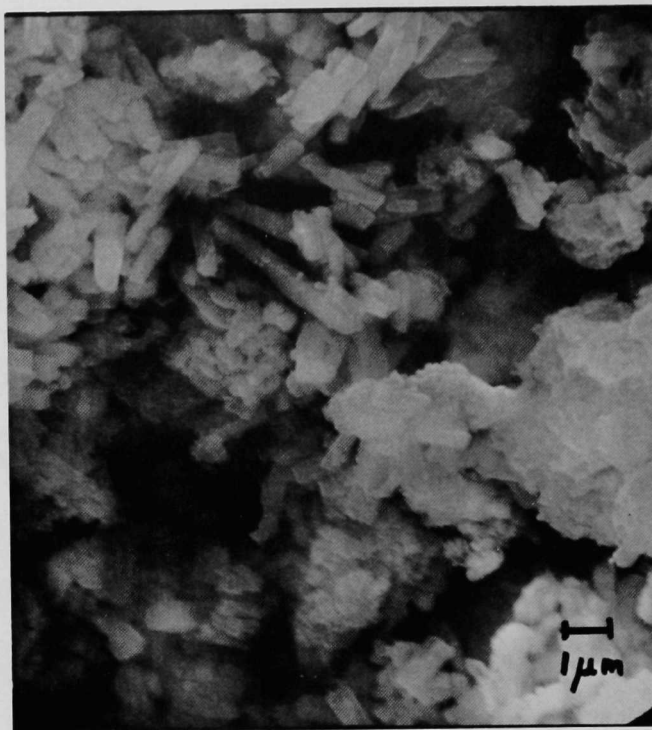


Fig. 1. Scanning Electron Micrograph of LiAlO_2 in Sample 98-18 (see Table 1 for description)

A third sample (98-14) was prepared from a CO_2 -treated physical mixture of $\text{LiOH/KOH}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ at 296 and 773 K. To prepare 98-14, $\gamma\text{-Al}_2\text{O}_3$ was slurried in a LiOH/KOH solution which contained only one-third of the stoichiometric amount of LiOH necessary to completely convert $\gamma\text{-Al}_2\text{O}_3$ to LiAlO_2 . After the solution was evaporated to dryness, the powder was ground, sieved ($<149\text{ }\mu\text{m}$), and then mixed with the necessary amount of $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (62 mol % Li_2CO_3 -38 mol % K_2CO_3). In this sample, $\beta\text{-LiAlO}_2$ was found to be the major phase by X-ray diffraction, and a few additional X-ray diffraction lines suggested the presence of a minor amount of an amorphous phase. Scanning electron microscopic analysis showed that very few rod-shaped particles were present (see Fig. 2). Instead, the prevalent particle shape was that of a rhomboidal prism, with particle sizes of about $1\text{ }\mu\text{m}$. Apparently, the experimental conditions were not favorable for the formation of $\beta\text{-LiAlO}_2$ rodlike particles. Perhaps this is due to the relatively high concentration of $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ in the starting sample, which increases the liquidus temperature so that the fluid environment necessary for the growth of rodlike LiAlO_2 particles is not achieved during CO_2 treatment at room temperature.

Sample 98-7 has been hot pressed in an electrolyte structure (tile) and tested in a molten carbonate fuel cell (CS-8). The other two samples will be hot-pressed and tested in the near future.

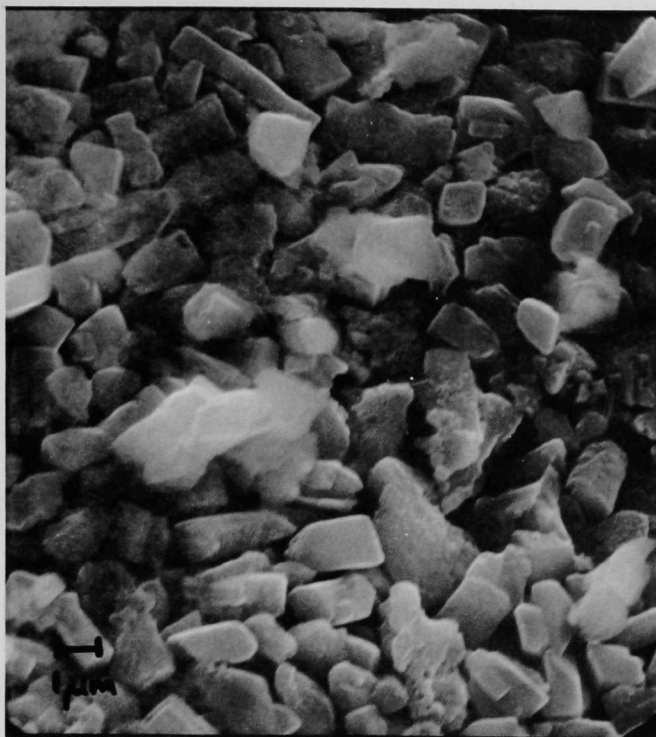


Fig. 2. Scanning Electron Micrograph of LiAlO_2 in Sample 98-14 (see Table 1 for description)

Fuel cells with electrolyte tiles containing only rodlike particles of $\beta\text{-LiAlO}_2$ have exhibited poorer performance than cells with $\alpha\text{-LiAlO}_2$ tiles. Post-test analyses of these fuel cells have showed that the tiles containing rodlike LiAlO_2 had a high porosity within the wet seal area, which is generally not as pronounced in tiles containing finer particles of LiAlO_2 . The porosity may be an artifact of the synthesis method; for example, complete conversion of the hydroxides to carbonates in the $\text{LiOH/KOH}/\gamma\text{-Al}_2\text{O}_3$ was not achieved even though a differential thermal analysis showed a liquidus temperature of ~ 763 K after exposure of the sample to CO_2 at 873 K. To check this possibility, electrolyte samples containing rodlike particles of $\beta\text{-LiAlO}_2$ were slurried in acetic acid-acetic anhydride to remove the alkali carbonates and any alkali hydroxides that may have been present. The liquid was decanted, and the solid material was washed with methanol and dried. The isolated $\beta\text{-LiAlO}_2$ particles will be mixed with $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ that is free of alkali hydroxides, pressed into an electrolyte structure and tested in a molten-carbonate fuel cell to evaluate effects due to residual hydroxide or other impurities.

In one treatment, a water wash rather than a methanol wash was used. X-ray diffraction analysis of the water-washed LiAlO_2 sample showed the presence of hydrated LiAlO_2 ($\text{Li}_2\text{Al}_2\text{O}_4 \cdot y\text{H}_2\text{O}$) as well as $\beta\text{-LiAlO}_2$. Although heating the sample in air at 398 K for about 72 h converted the hydrated LiAlO_2 back to $\beta\text{-LiAlO}_2$, the material was no longer of the rodlike form, but appeared to consist of a variety of particle shapes, as shown in the scanning electron micrograph in Fig. 3. In addition to the rodlike

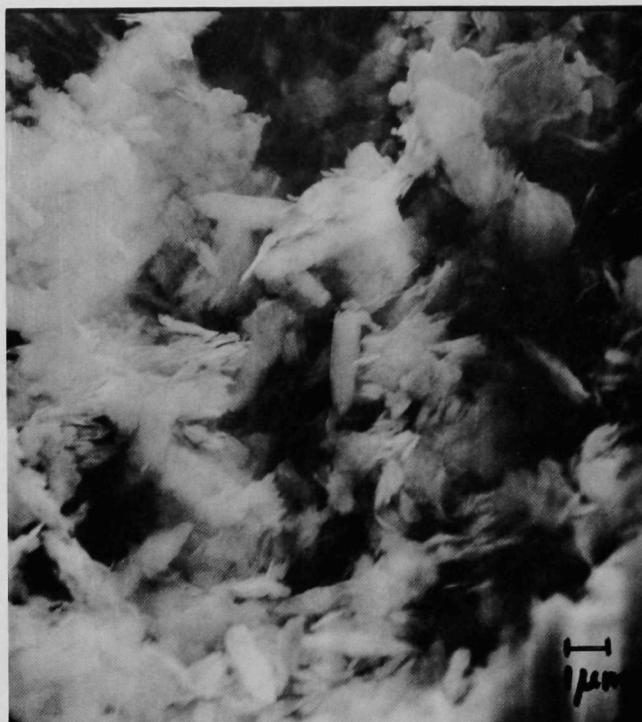


Fig. 3. Scanning Electron Micrograph of β - LiAlO_2 After Removal of Alkali Carbonates and Heat Treatment at 398 K for 92 h

particles, clumps and small "flake-like" particles are present. This material appears suitable for use in tiles, and will be mixed with $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ and tested as an electrolyte tile in a molten carbonate fuel cell.

It is clear that β - LiAlO_2 is unstable to hydrolysis in (acidic) aqueous media, and for analytical purposes should be kept free of excess water. The relative amounts of acetic acid, acetic anhydride, and LiAlO_2 /alkali carbonate are important in ensuring that the LiAlO_2 particles do not undergo reaction with dissolved species (water) in solution. Based on our experience with the isolation of LiAlO_2 for SEM analysis, it is recommended that the ratio of acetic acid-acetic anhydride to electrolyte be kept high (see Appendix for procedure). A large excess of acetic anhydride will react with the product water as it forms, preventing hydrolysis of LiAlO_2 , with consequent formation of $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2$ and hydrated LiAlO_2 .

B. Phase and Structural Stability of LiAlO_2

Studies of the phase and structural stability of rodlike β - LiAlO_2 particles at 923 K in gas environments simulating molten carbonate fuel cell conditions have been extended to 2400 h. Powder samples of β - LiAlO_2 (45 wt %, 61 vol %)* mixed with $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ (composition, 62 mol % Li_2CO_3 -38 mol % K_2CO_3) were examined by X-ray diffraction and SEM during a period of 2400 h in 78% H_2 /19% CO_2 /3% H_2O and also during 2585 h in air. In both experiments, the original rodlike β - LiAlO_2 particles have remained unchanged in phase and particle shape. Although the lengths of these β - LiAlO_2

* All values for volume percentages of tile constituents in this report are based on the volume of Li_2CO_3 - K_2CO_3 at 923 K.

stability tests are only a small fraction of the goal lifetime (40,000 h) for the commercial molten-carbonate fuel cell, our studies suggest that the long-term performance decay of the fuel cell at 923 K will probably be due mainly to other factors (*e.g.*, anode-sintering and electrolyte loss), and not the structural stability of β -LiAlO₂ in the electrolyte tile.

The results obtained on the stability of the powder samples of β -LiAlO₂ in the controlled-environment tests were substantiated in short-term fuel cell tests with electrolyte tiles containing rodlike β -LiAlO₂. Scanning electron microscopic analyses of the LiAlO₂ in fuel cells CS-5 and CS-6 after 736 and 654 h, respectively, at 923 K showed that the original β -LiAlO₂ particles remained unchanged in phase and particle shape.

III. CELL TESTING

The primary objective of cell testing at ANL is to understand and control significant properties of the cell components and the changes in these properties during cell operation. Areas which have received particular attention are corrosion of the wet-seal area of the cell housings and the effects on cell performance of different types of LiAlO₂ filler material in the electrolyte tile. A process of flame-spraying aluminum onto the wet-seal area of the cell housings, followed by heating at 1275 K (*in vacuo* or in an atmosphere of helium) appears to produce a dense, strongly bonded layer of protective aluminum (which may transform to Al₂O₃ and then to LiAlO₂ when in contact with the electrolyte). The tiles containing only rod-shaped β -LiAlO₂ (relatively uniform in size, ~ 4 μ m long by ~ 0.7 μ m dia) appear to be less effective in retaining alkali carbonates than similar tiles containing clump-shaped α -LiAlO₂. This reduced retention leads to dimensional instability of the electrolyte tile, creeping of the alkali carbonates around the cell housings, flooding of the electrodes with electrolyte, and poor cell performance.

A. Cell Operation

During this quarter, operation of the CS-series of cells was continued with Cells CS-5 through CS-8. The characteristics of these cells are shown in Table 2. Cells CS-1 through CS-4 were operated during the previous quarter, and details of their construction can be found in the preceding quarterly report (ANL-77-56, pp. 6-9).

The most significant difference between the cells with high performance (CS-1 and CS-7) and the other cells was the electrolyte tile. The tiles in Cells CS-1 and CS-7 were prepared from γ -Al₂O₃ (Degussa Type C), Li₂CO₃, and K₂CO₃ at 873 K, and contained a relatively large range of sizes of α -LiAlO₂ particles of the ill-defined morphology designated as "clumps." These tiles generally held their shape very well during operation. The tiles used in Cells CS-2 through CS-6, on the other hand, were made from rod-shaped β -LiAlO₂ particles which were uniform in size and shape (~ 4 μ m long x 0.7 μ m dia), and these tiles were soft and easily deformed.

The previous work (ANL-77-56) showed that the performance differences between CS-1 and CS-2 through -4 were not closely related to differences in electrodes or in construction details, but rather to the electrolyte tile.

Table 2. Characteristics of Cells CS-5 Through CS-8^a

	CS-5	CS-6	CS-7	CS-8
Electrolyte Tile				
Thickness, cm	0.19-0.20	0.20-0.22	0.19-0.21	0.19-0.22
Alkali Carbonates, wt % (vol %)	60(66)	60(66)	55(68)	55(64)
LiAlO ₂ Phase	β	β	α (maj); γ, β (min)	α, β (maj); γ (min)
LiAlO ₂ Morphology	rods	rods	clumps	clumps + rods
Cell Resistance, m Ω	72	26	28	37
Maximum Cell Voltage, V, at 40 mA/cm ² (38% utilization)				
IR included	0.745	0.765	0.891	0.741
IR free	0.827	0.794	0.923	0.783
Total Operating Time, h	736	654	698	601

^aAnodes: Gould 309-144-3 material rolled to 0.043-cm thickness from 0.076 cm; porosity, 84%; mean pore size, 10 μ m (quoted by manufacturer for unrolled material).

Cathodes: Union Carbide 306-24-30B material of 0.064-cm thickness; porosity 71.5%; mean pore size, 6.6 μ m (determined by mercury porosimetry data).

After operation of Cell CS-4, consideration of the density difference between α -LiAlO₂ (ρ = 3.4) and β -LiAlO₂ (ρ = 2.6) led us to increase the carbonate content of the tiles. The tiles of Cells CS-5 and CS-6 (see Table 2) therefore had carbonate contents of 60 wt % (66 vol %), rather than the 55 wt % (61 vol %) used in the tiles of Cells CS-2 through -4. The effect of this change was to exacerbate the problem of poor performance for the first few hundred hours of cell operation; thereafter, the performance of Cells CS-5 and CS-6 gradually increased to the level of CS-2, -3 and -4 (see Figs. 4 and 5) after 150-400 h.

Our present operating hypothesis is that tiles made with LiAlO₂ of uniform size and shape hold molten carbonate less tenaciously than tiles with a wide distribution of LiAlO₂ particle sizes, presumably because of a large mean pore size in the tile, and a narrow pore-size distribution. This would also be reflected in a weaker structural cohesive force. Electrodes in contact with tiles made from uniform LiAlO₂ particles would extract too much, not too little, liquid carbonate from the tile. This hypothesis is supported by the behavior of CS-5 and 6, which took several hundred hours to achieve the level of performance shown by Cells CS-2 through -4. It appears that the excess electrolyte is lost by seepage from the tile followed by reaction with the exteriors of the cell housings. This mode of loss was not observed in Cells CS-1 and CS-7.

The presence of at least some long narrow particles (such as the rodlike β -LiAlO₂ particles) is regarded as being beneficial to tile integrity and strength, whereas we have clearly shown that an aggregate of particles homogeneous in size and shape is undesirable. Investigation of the performance and properties of tiles formed from mixtures of rodlike β -LiAlO₂ and α -LiAlO₂ clumps is clearly required, and this is being undertaken

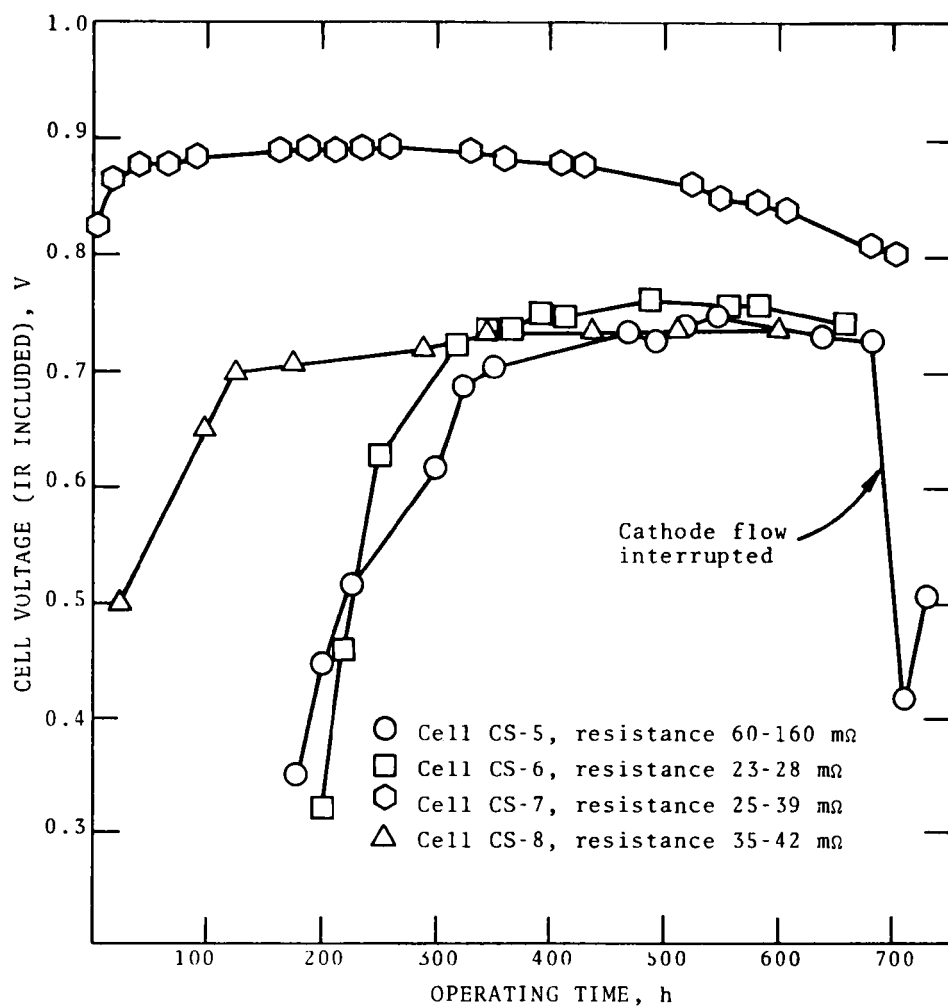


Fig. 4. Performance vs. Operating Time for Cells CS-5, CS-6, CS-7, and CS-8 [923 K; current density, 40 mA/cm² (38% utilization)]

(see Section II. A). The tile of Cell CS-8 was the first of these to be tested. However, its performance is suspect because of inadvertent thermal cycling during startup. The CS-8 tile showed the same type of deformation as the tiles of Cells CS-2 through CS-6, which contained only β -LiAlO₂.

Another experiment to test the hypothesis is under way. The rodlike β -LiAlO₂ is being separated from a mixture of the type used to prepare the tiles of Cells CS-2 through CS-6, and mixed with the Li₂CO₃ and K₂CO₃ used to prepare the tiles of Cells CS-1 and CS-7 (see Section II.A). A tile pressed from this mixture will be evaluated and operated in a cell to check the possibility that some component other than the LiAlO₂ is responsible for the observed differences, perhaps by altering the electrolyte wetting properties.

Cell CS-7, which has a tile containing α -LiAlO₂ of wide particle-size distribution, has shown the best performance of any cell operated to date (see Fig. 6). As a check on performance, and for easier comparison with other

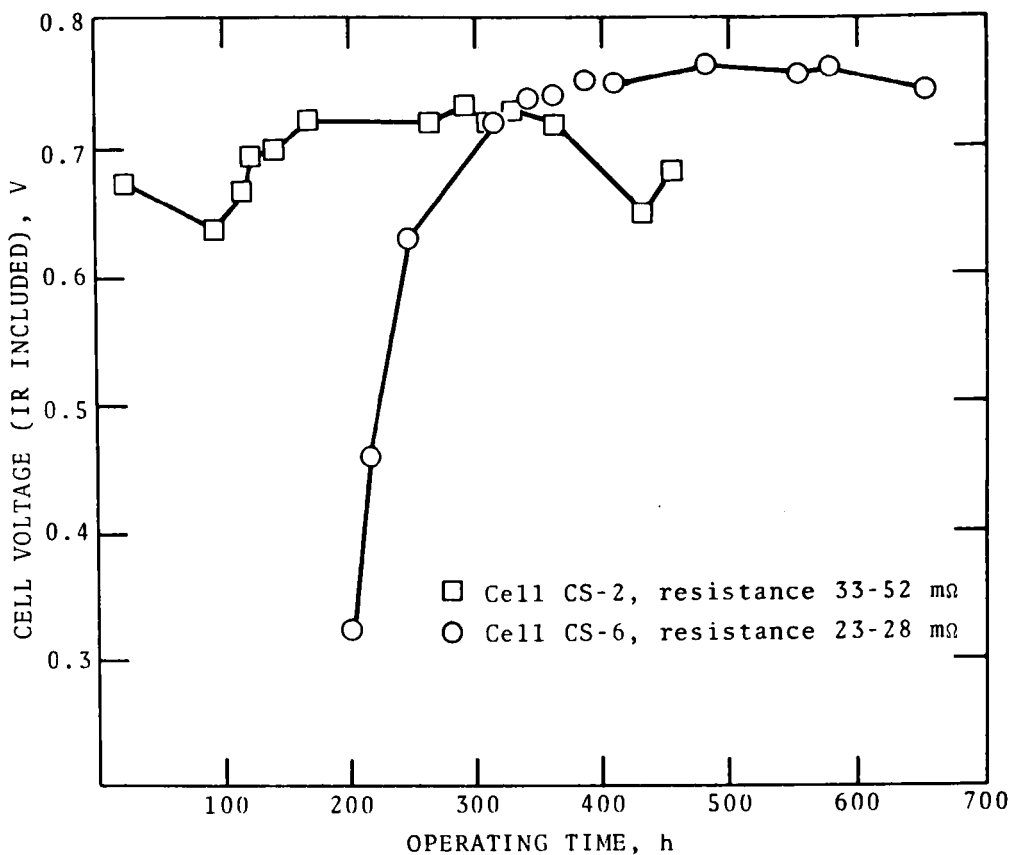


Fig. 5. Performance vs. Operating Time for Cells CS-2 and CS-6 [923 K; current density, 40 mA/cm² (38% utilization)]

contractors' cells, the cell was operated at current densities from 170 to 210 mA/cm² and 10-A flows of both fuel (wet 80% H₂/20% CO₂) and oxidant (dry 70% air/30% CO₂). Since the cell area is 28.56 cm², this represents conversions of 48.5-60% at both anode and cathode. Under these conditions, the power density was in excess of 110 mW/cm².

The objectives of all ANL cell operations to date are to study and improve cell components, not to maximize performance for its own sake. Nonetheless, geometry of the cells (round for CS- and KK- series) will soon be changed, and a square cell having better-defined gas and current distributions will be used in the cell tests.

B. Wet-Seal Protection

Two sets of cell housings with protected wet seals have been tested in the CS-series cells. The method of protection involves flame-spraying* of aluminum onto the wet seal to a depth of ~50-70 μm and heating (*in vacuo*

* Flame-spraying was performed by Coating Systems Technology, North Babylon, NY.

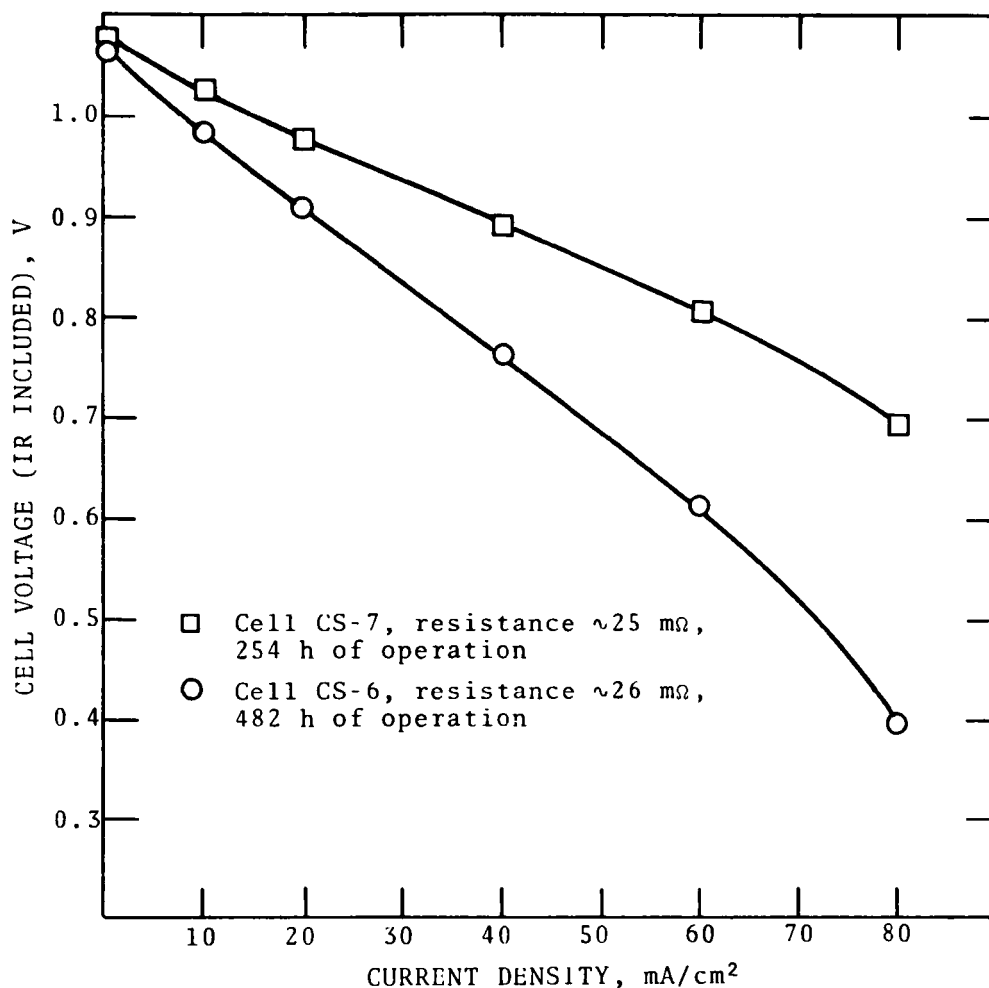


Fig. 6. Best Performance of Cells CS-6 and CS-7 (923 K, 3A flows, 28.56 cm² electrode area)

or in helium) to 1275 K for ~30 min to form a diffused layer between the aluminum and the Type 316 stainless steel substrate. During initial cell operation, the aluminum is converted to Al₂O₃ or LiAlO₂ by reaction with the electrolyte.

Two sets of electrode housings (anode and cathode) have been used for the CS-series cell tests. One set was used for Cells CS-1, -2, -3, -5, and -7, for a total operating time of 2628 h. The only significant corrosion observed was pitting of the anode housing at the edges of the wet-seal area, which were not completely covered with aluminum (see Fig. 7). The corrosion was barely noticeable until after the test of Cell CS-7, *i.e.*, until after the housing had been used for 2628 h. The second set of housings has been used for Cells CS-4, -6, and -8, for a total operating time of 1495 h. Thus far, no significant amount of corrosion has been observed.

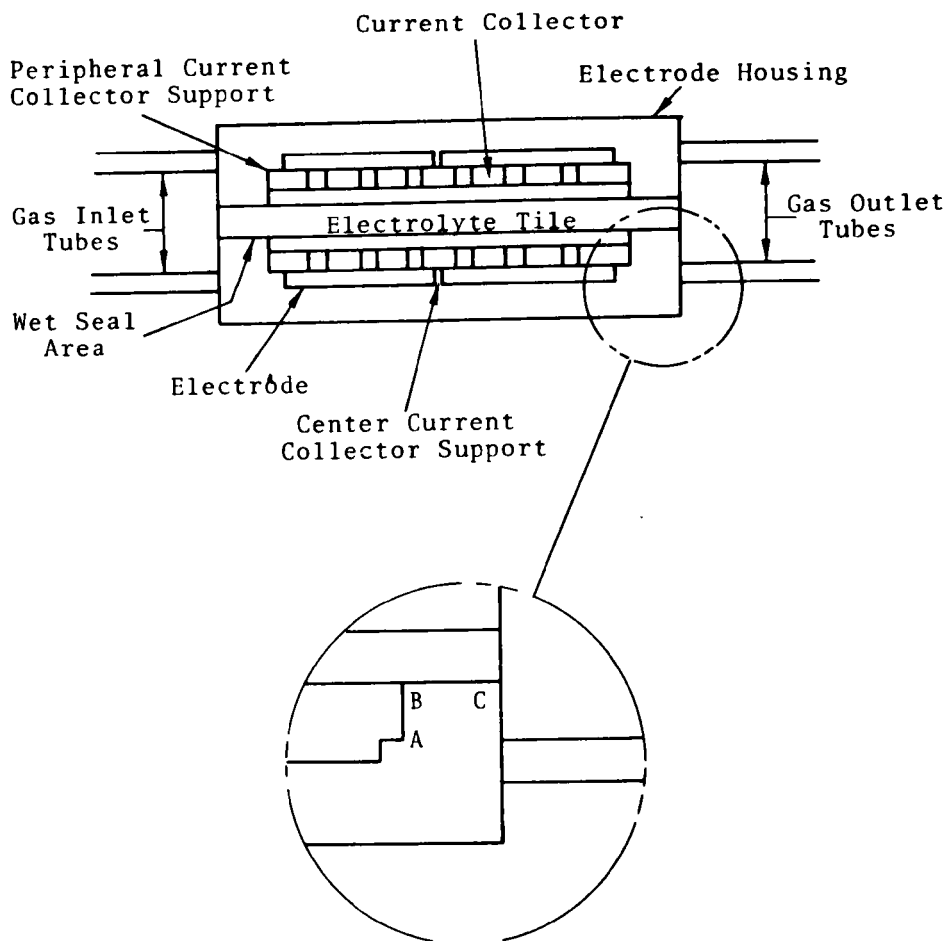


Fig. 7. Diagram of Cell Housings Showing Areas of Wet-Seal Corrosion (Pitting occurred at B and C and along segment AB. Segment BC, which was protected by aluminum, was corrosion-free.)

Corrosion of the edges of the wet seal could probably be eliminated by carefully flame-spraying these areas with aluminum. Moreover, the corrosion observed in this area may be less serious than it appears. Because of seepage of alkali carbonates from the electrolyte tiles tested in these cell housings, substantial creeping of carbonates over the corroded area occurred. A tile which effectively retains the corrosive carbonates should minimize contact of the carbonates with this area of the wet seal and thereby reduce corrosion.

IV. COMPONENT ANALYSIS AND DIAGNOSTICS

A. Tile Diagnostics

During this quarter, static creep measurements were made on specimens of a tile containing 54 wt % (48 vol %) β -LiAlO₂ and 46 wt % (52 vol %) of the lithium-rich eutectic (62 mol % Li₂CO₃-38 mol % K₂CO₃); the β -LiAlO₂ had a clump-type morphology. The measurements were conducted for 38 days (912 h) in a CO₂ environment with a load of 93 kPa (13.5 psi) at a temperature of 923 K. The results are shown in Fig. 8. In 912 h the specimen showed a static creep of 0.072 mm, which corresponds to approximately 1% of the 6.67-mm specimen thickness. The curve indicates that the rate of change in thickness is decreasing with time, *i.e.*, the greatest deformation (or creep) of the specimen occurred in the first 500 h; thereafter the rate of creep became rather small.

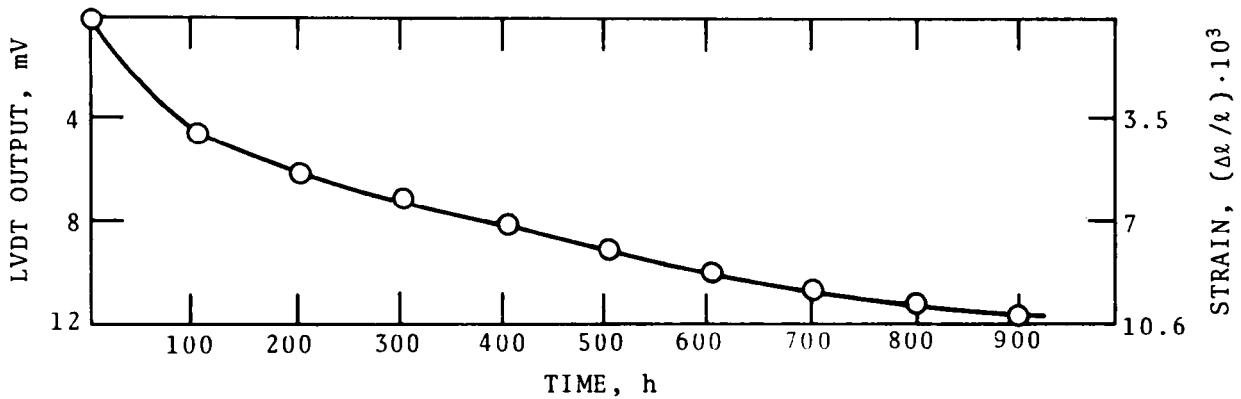


Fig. 8. Creep Behavior of Tile Containing 54 wt % β -LiAlO₂ of Clump-Type Morphology (Measurements made at 923 K, 93 kPa in a CO₂ environment; LVDT = linear voltage differential transducer)

A typical high-temperature creep curve for polymeric or crystalline materials generally has three distinct regions:¹ 1) primary or decelerating creep, 2) secondary or steady-state creep and 3) tertiary or accelerating creep. Low-temperature creep, on the other hand, is considered to have only a decelerating stage. At low temperatures, an empirical equation, first suggested by Andrade,^{2,3} for the creep behavior of polymeric and crystalline materials reduces to

$$\gamma = \beta t^{1/3} \quad (1)$$

where γ is the strain in time t and β is a constant. Analysis of the experimental data in Fig. 8 indicates that the creep behavior is still in the primary region (decelerating). This is evident in Fig. 9, where

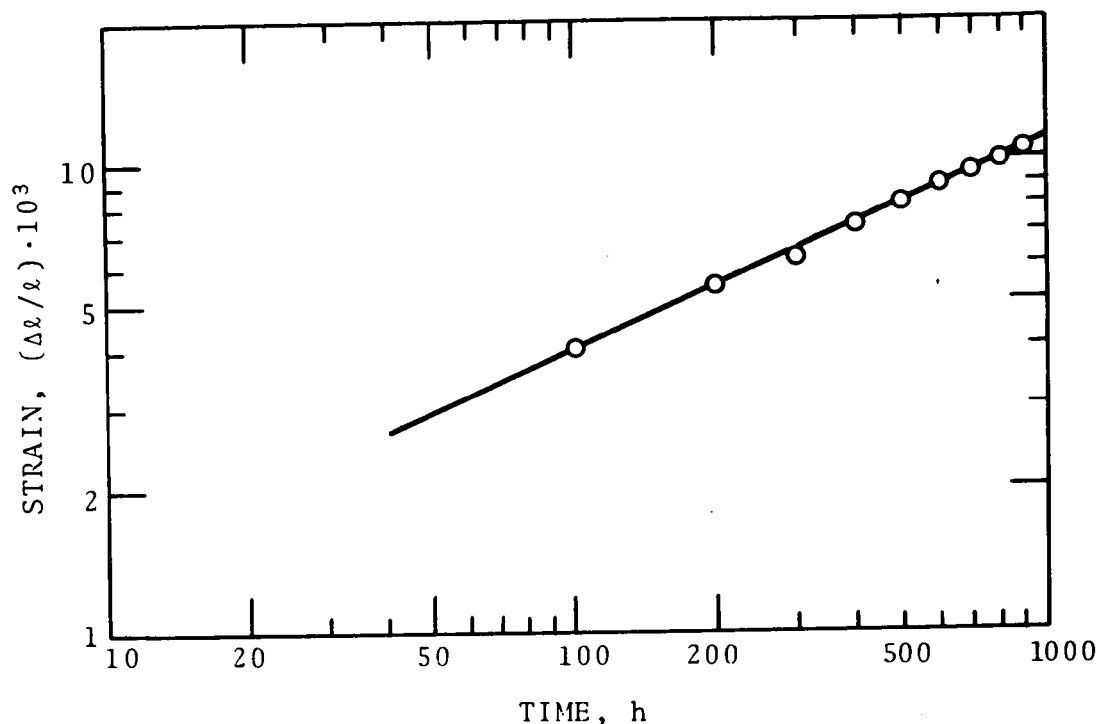


Fig. 9. Log-Log Plot of Creep Data from Fig. 8

the data from Fig. 8 are plotted on a log-log scale. The equation corresponding to the curve in Fig. 9 is

$$\gamma = 0.6t^{1/2.5} \quad (2)$$

This equation is similar to the reduced form of Andrade's equation for low-temperature decelerating creep.

The average creep rate during the first 200 h at 923 K for the specimen of electrolyte tile plotted in Fig. 8 is $26 \times 10^{-6} \text{ h}^{-1}$. This value is similar to the values previously observed (ANL-77-56, p. 14), namely, 36×10^{-6} and $30 \times 10^{-6} \text{ h}^{-1}$, for specimens obtained from the same electrolyte tile.

Creep measurements at 923 K were also conducted on part of a tile containing 45 wt % (32 vol %) $\alpha\text{-LiAlO}_2$ and 55 wt % (68 vol %) alkali carbonates (62 mol % Li_2CO_3 -38 mol % K_2CO_3). The average creep rate during the first 200 h was approximately $67 \times 10^{-6} \text{ h}^{-1}$ which is considerably lower than the value ($945 \times 10^{-6} \text{ h}^{-1}$) reported in the preceding quarterly report (ANL-77-56, p. 14) on another sample of the same electrolyte tile. However, this latter value was obtained by extrapolation of the data measured between 873 and 973 K over a period of 50 h and should be disregarded in view of the more recent measurement made at constant temperature.

B. Corrosion Studies

During this quarter a cell (RS-1) was clad with Type 310 stainless steel foil (0.125-mm thick) and operated for 200 h at 923 K. The discharge current density was maintained at approximately 70 mA/cm², and the cell voltage was 0.825 V during the entire cell operation. The electrolyte tile used in the cell contained 45 wt % (39 vol %) β -LiAlO₂ (clump-shaped particles) and 55 wt % (61 vol %) alkali carbonates (62 mol % Li₂CO₃, 38 mol % K₂CO₃). Anode and cathode gas flows were both maintained at 3 A. Anode and cathode gases were 80% H₂/20% CO₂, and 27% CO₂/15% O₂/58% N₂, respectively.

After operation of the cell was discontinued, examination of the foils showed that corrosion was mainly at the wet-seal areas. As previously observed with other cells having unprotected wet seals (no aluminized coating to prevent wet-seal corrosion), corrosion at the anodic wet-seal areas was uniform and extensive, while at the cathode it was not so severe and was intermittent, as shown in Fig. 10. The scanning electron micrographs show that the maximum average depths of corrosion at the anode and cathode wet-seal areas, respectively, were approximately 30 and 8 μ m. The wet-seal areas of both electrodes showed zones of diffused corrosion resulting from intergranular attack; corrosion in these zones is included in the values for maximum average depths of corrosion. Assuming that the corrosion rate is linear up to 40,000 h, the maximum extent of corrosion in Type 310 stainless steel would be 6 mm at the anode, while at the cathode it would be no more than 1.6 mm. These values are higher than would be expected because corrosion would be much more likely to proceed at a parabolic rate or might be negligible once the iron and chromium oxide films are formed on the metal surfaces. Table 3 summarizes the results obtained by the complementary

Table 3. Analysis of Corrosion Products

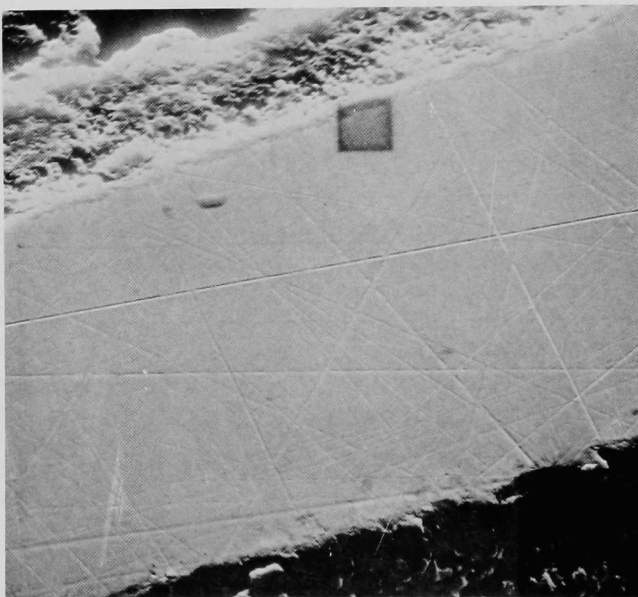
Location	Depth of Corrosion, μ m	X-Ray Diffraction Results (Color of Corrosion Product)	SEM-EDXA Results ^a
Cathode Wet-Seal Area	~8	α -LiFeO ₂ (red) LiCrO ₂ (black) α -K ₂ CrO ₄ (yellow)	Fe, Cr, K, Al
Anode Wet-Seal Area	~30	α -LiFeO ₂ (red) LiCrO ₂ (black)	Cr, Fe, Ni K, Al

^aAl is from embedded LiAlO₂; K is most likely from K₂CrO₄ or K₂CO₃; Ni could be present as NiO, but NiO could not be detected by X-ray analysis; Fe and Cr are from the Type 310 stainless steel.

techniques of X-ray diffraction and SEM-EDXA (energy-dispersive X-ray analysis). It is apparent that protective coatings consisting of LiCrO₂ and LiFeO₂ were formed on the cathode, as well as anode, wet-seal areas.



(A) Cathode Cladding (600X)



(B) Anode Cladding (550X)

Fig. 10. Scanning Electron Micrographs of Type 310 Stainless Steel Cladding Showing Corrosion in the Wet-Seal Areas after 200 h of Cell Operation

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2. E. Andrade, Proc. Roy. Soc. London Ser. A 84, 1 (1910).
3. *Ibid*, Ser. A 90, 329 (1914).

APPENDIX

Procedure for Removing Carbonate from LiAlO_2

The electrolyte powder sample (~100 mg of a mixture of LiAlO_2 + alkali carbonates) is added to 100 ml of 70:30 vol % glacial acetic acid/acetic anhydride and ultrasonically agitated until the LiAlO_2 powder is in suspension (usually less than 5 min). The sample is then allowed to settle, the supernatant liquid is removed, and about 100 ml of absolute methanol is added to wash the LiAlO_2 particles. After ultrasonic agitation to form a suspension, the LiAlO_2 particles are allowed to settle and the methanol is removed. The LiAlO_2 sample is then transferred to a desiccator and vacuum-dried at room temperature.

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